

Breakdown of Chemical Scaling for Pt-Doped CaFe_2As_2

Kazutaka KUDO^{1,2*}, Masakazu KOBAYASHI^{1,2}, Satomi KAKIYA^{1,2}, Masataka DANURA^{1,2}, and Minoru NOHARA^{1,2}

¹*Department of Physics, Okayama University, Okayama 700-8530, Japan*

²*JST, Transformative Research-Project on Iron Pnictides (TRIP), Chiyoda, Tokyo 102-0075, Japan*

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The electronic phase diagram of Co-doped CaFe_2As_2 captures the generic features of iron-based superconductors.^{1–3} The parent compound CaFe_2As_2 exhibits a phase transition from a paramagnetic metal (PM) phase to an antiferromagnetic metal (AFM) one upon cooling at a transition temperature $T_N = 170$ K, as shown in Fig. 1(a).⁴ Almost simultaneously, system exhibits a structural phase transition from a tetragonal phase to an orthorhombic one at T_s .⁴ The partial chemical substitution of Co for Fe suppresses the AFM and orthorhombic phase, and a superconducting phase appears. The maximum superconducting transition temperature $T_c = 20$ K is observed near the critical concentration of Co, i.e., $x \simeq 0.06$, at which the AFM ordering is completely suppressed in $\text{Ca}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$.⁴ The superconducting phase disappears on further doping. Ni-doped CaFe_2As_2 shows similar phase diagram;⁵ however, the critical concentration of Ni, at which the AFM phase is suppressed and superconducting phase appears, is almost half of that for Co-doped CaFe_2As_2 , as shown in Fig. 1(a). The above-mentioned observations imply that the dependence of T_N , T_s , and T_c on the doping level x can be interpreted in terms of the difference in the number of valence electrons between the doped transition metal (TM) and iron,^{6,7} namely, the chemical scaling of the electronic phase diagram. Such scaling has been reported for SrFe_2As_2 as well as BaFe_2As_2 with different TMs.^{6,7}

In this paper, we report a breakdown of the scaling of T_N on chemical doping x for Pt-doped CaFe_2As_2 . We demonstrate that the AFM phase persists until the Pt content x reaches its solubility limit at 0.08. This behavior is contradictory to that of Ni-doped CaFe_2As_2 , in which the AFM is suppressed at $x = 0.03$, although both Ni and Pt are

*E-mail address: kudo@science.okayama-u.ac.jp

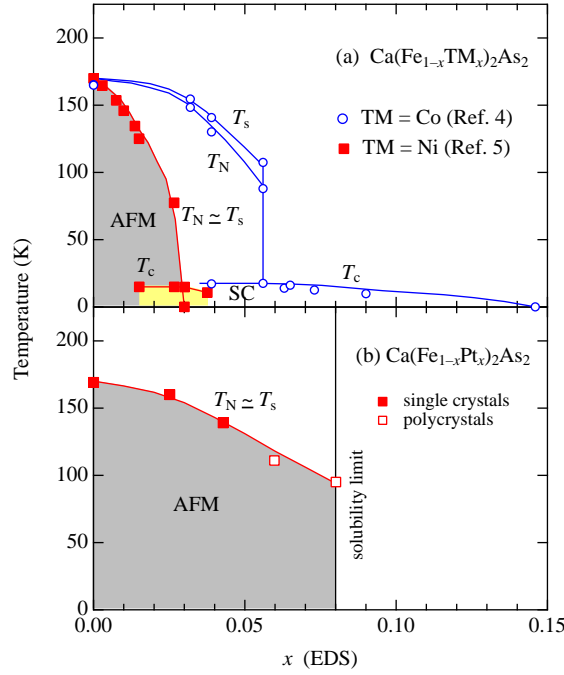


Fig. 1. (Color online) (a) Electronic phase diagrams of $\text{Ca}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ ⁴ and $\text{Ca}(\text{Fe}_{1-x}\text{Ni}_x)_2\text{As}_2$.⁵ AFM and SC denote antiferromagnetic and superconducting phases, respectively. T_N , T_S , and T_c denote the AFM transition temperature, structural phase transition temperature, and superconducting transition temperature, respectively. (b) Electronic phase diagram of $\text{Ca}(\text{Fe}_{1-x}\text{Pt}_x)_2\text{As}_2$. The closed and open squares indicate T_N determined from magnetization measurements using single crystals and polycrystals, respectively.

isovalent. Thus, we observe that $\text{Ca}(\text{Fe}_{1-x}\text{Pt}_x)_2\text{As}_2$ does not exhibit superconductivity.

Single crystals of $\text{Ca}(\text{Fe}_{1-x}\text{Pt}_x)_2\text{As}_2$ ($x = 0, 0.025$, and 0.043) were grown using a self-flux method. Details of this method are given in Ref. 8. Polycrystalline samples of $\text{Ca}(\text{Fe}_{1-x}\text{Pt}_x)_2\text{As}_2$ ($x = 0.06$ and 0.08) were synthesized by a solid-state reaction.⁹ Prescribed amounts of Ca, FeAs, Pt, and As powders or grains were mixed and ground. The resulting powder was heated in an evacuated quartz tube at 700°C for 3 h and then at 1000°C for 72 h. The obtained samples were characterized by powder X-ray diffraction (XRD) and confirmed to be a single phase of $\text{Ca}(\text{Fe}_{1-x}\text{Pt}_x)_2\text{As}_2$. The Pt content x was determined by energy dispersive X-ray spectrometry (EDS); we used this value of x in the study. The maximum value of x obtained by the self-flux growth was approximately 0.043. The range of x could be extended up to 0.08 through a solid-state reaction. A single-phase sample with x greater than 0.08 was hardly obtained, indicating that the solubility limit of Pt was at $x = 0.08$ in $\text{Ca}(\text{Fe}_{1-x}\text{Pt}_x)_2\text{As}_2$.

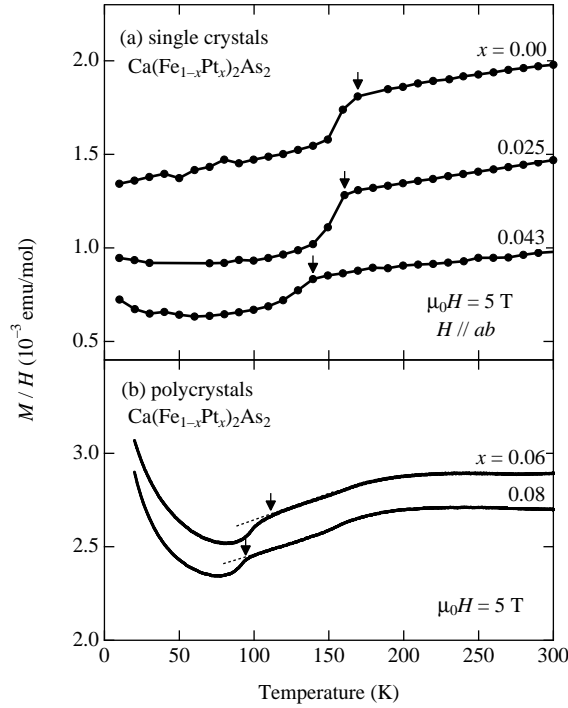


Fig. 2. Temperature dependence of magnetization divided by magnetic field, M/H , for (a) single crystals and (b) polycrystals of $\text{Ca}(\text{Fe}_{1-x}\text{Pt}_x)_2\text{As}_2$ in a magnetic field of 5 T. The arrows indicate the antiferromagnetic transition temperature T_N . For clarity, M/H is shifted by $+0.8 \times 10^{-3}$ emu/mol and $+0.4 \times 10^{-3}$ emu/mol for $x = 0.00$ and 0.025 , respectively. Broken lines in (b) are guides to the eye.

We measured magnetization M using a SQUID magnetometer (Quantum Design). The magnetic susceptibility M/H of single crystals exhibited a characteristic T -linear behavior in the paramagnetic phase at high temperatures, indicative of magnetic fluctuations,^{8,10} and subsequently, M/H decreased rapidly at the antiferromagnetic transition temperature T_N ,⁸ indicated by arrows in Fig. 2(a). We expect that a structural phase transition occurs at $T_s \simeq T_N$, although T_s and T_N were hardly resolved from the M/H data.¹¹ A similar behavior of M/H was observed in the polycrystalline samples, as shown in Fig. 2(b), although these samples show a tiny Curie tail at low temperatures, that is superposed with an almost temperature independent background (of approximately 2×10^{-3} emu/mol), most probably due to tiny impurities in them. No sign of superconductivity is observed in the low-field magnetization (not shown). The electronic phase diagram of $\text{Ca}(\text{Fe}_{1-x}\text{Pt}_x)_2\text{As}_2$ is obtained on the basis of this data, as shown in Fig. 1(b). The antiferromagnetic transition temperature T_N (as well as T_s) decreases with increasing x , as is generally observed in iron-based superconductors upon

chemical doping. However, T_N (and T_s) decreases at a slow rate, and the AFM phase remains intact until x attains the solubility limit at 0.08. Thus, superconductivity does not emerge in $\text{Ca}(\text{Fe}_{1-x}\text{Pt}_x)_2\text{As}_2$.

The difference in phase diagrams between Ni and Pt doped CaFe_2As_2 is striking. Ni and Pt are isovalent, i.e., both have the same number of valence electrons. Therefore, it would be obvious to expect that Ni and Pt will dope almost the same amount of carriers, and thus, T_N (and T_s) will decrease with Ni and Pt doping at an almost same rate; therefore, the chemical scaling will hold. Indeed, in the case of SrFe_2As_2 , the AFM phase is suppressed at approximately the same doping level $x = 0.07$, for both Ni⁶ and Pt.^{9,12} At present, the question why the scaling breaks down in Pt-doped CaFe_2As_2 is, however, unanswered. In order to answer this question, further studies need to be conducted from the viewpoints of structural parameters,¹³ disorder,¹⁴ magnetic dilution,¹⁵ and first principles.^{16,17}

Finally, we note that a novel phase, $\beta\text{-Ca}_{10}(\text{Pt}_3\text{As}_8)(\text{Fe}_{2-x}\text{Pt}_x\text{As}_2)_5$ ($x = 0.16$), appears along with $\text{Ca}(\text{Fe}_{1-x}\text{Pt}_x)_2\text{As}_2$ ($x = 0.08$), when we intend to substitute Pt beyond the solubility limit at $x = 0.08$. Interestingly, the former exhibits superconductivity at $T_c = 13$ K,¹⁸⁻²⁰ whereas the latter does not, even though the Pt content of the Fe site is almost the same in both (8%). We expect the additional charge carriers (electrons) to be self-doped from the Pt_3As_8 layers to the FeAs layers of $\beta\text{-Ca}_{10}(\text{Pt}_3\text{As}_8)(\text{Fe}_{2-x}\text{Pt}_x\text{As}_2)_5$, although the compound is still in the underdoped region according to a Hall measurement.¹⁸ Further attempt to increase Pt concentration yields $\alpha\text{-Ca}_{10}(\text{Pt}_4\text{As}_8)(\text{Fe}_{2-x}\text{Pt}_x\text{As}_2)_5$ ($x = 0.36$), which exhibits superconductivity at a higher temperature of $T_c = 38$ K.¹⁸ The requirement of such a heavy doping of Pt to achieve superconductivity in $\alpha\text{-Ca}_{10}(\text{Pt}_4\text{As}_8)(\text{Fe}_{2-x}\text{Pt}_x\text{As}_2)_5$ is consistent with the inefficiency of Pt in reducing the AFM phase of CaFe_2As_2 .

In conclusion, we found that the substitution of Pt is ineffective in the reduction of AFM ordering as well as in inducing superconductivity in $\text{Ca}(\text{Fe}_{1-x}\text{Pt}_x)_2\text{As}_2$, and the chemical scaling of the electronic phase diagram breaks down. The Pt-doped CaFe_2As_2 that does not exhibit superconductivity will, however, provide us an ideal opportunity to elucidate the role of chemical doping in the occurrence of superconductivity in iron-based materials.

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References

- 1) K. Ishida, Y. Nakai, and H. Hosono: J. Phys. Soc. Jpn. **78** (2009) 062001.
- 2) J. Paglione and R. L. Greene: Nature Phys. **6** (2010) 645.
- 3) D. C. Johnston: Adv. Phys. **59** (2010) 803.
- 4) L. Harnagea, S. Singh, G. Friemel, N. Leps, D. Bombor, M. Abdel-Hafiez, A. U. B. Wolter, C. Hess, R. Klingeler, G. Behr, S. Wurmehl, and B. Büchner: Phys. Rev. B **83** (2011) 094523.
- 5) N. Kumar, S. Chi, Y. Chen, K. G. Rana, A. K. Nigam, A. Thamizhavel, W. Ratcliff II, S. K. Dhar, and J. W. Lynn: Phys. Rev. B **80** (2009) 144524.
- 6) S. R. Saha, N. P. Butch, K. Kirshenbaum, and J. Paglione: Phys. Rev. B **79** (2009) 224519.
- 7) N. Ni, A. Thaler, A. Kracher, J. Q. Yan, S. L. Budfko, and P. C. Canfield: Phys. Rev. B **80** (2009) 024511.
- 8) M. Danura, K. Kudo, Y. Oshiro, S. Araki, T. C. Kobayashi, and M. Nohara: J. Phys. Soc. Jpn. **80** (2011) 103701.
- 9) Y. Nishikubo, S. Kakiya, M. Danura, K. Kudo, and M. Nohara: J. Phys. Soc. Jpn. **79** (2010) 095002.
- 10) G. M. Zhang, Y. H. Su, Z. Y. Lu, Z. Y. Weng, D. H. Lee, and T. Xiang: Europhys. Lett. **86** (2009) 37006.
- 11) D. K. Pratt, W. Tian, A. Kreyssig, J. L. Zarestky, S. Nandi, N. Ni, S. L. Bud'ko, P. C. Canfield, A. I. Goldman, and R. J. McQueeney: Phys. Rev. Lett. **103** (2009) 087001.
- 12) K. Kirshenbaum, S. R. Saha, T. Drye, and J. Paglione: Phys. Rev. B **82** (2010) 144518.
- 13) S. Drotziger, P. Schweiss, K. Grube, T. Wolf, P. Adelman, C. Meingast, and H. v. Löhneysen: J. Phys. Soc. Jpn. **79** (2010) 124705.
- 14) M. G. Vavilov and A. V. Chubukov: arXiv:1110.0972.
- 15) R. S. Dhaka, C. Liu, R. M. Fernandes, R. Jiang, C. P. Strehlow, T. Kondo, A. Thaler, J. Schmalian, S. L. Bud'ko, P. C. Canfield, and A. Kaminski: arXiv:1108.0711.
- 16) H. Wadati, I. Elfimov, and G. A. Sawatzky: Phys. Rev. Lett. **105** (2010) 157004.
- 17) K. Nakamura, R. Arita, and H. Ikeda: Phys. Rev. B **83** (2011) 144512.

- 18) S. Kakiya, K. Kudo, Y. Nishikubo, K. Oku, E. Nishibori, H. Sawa, T. Yamamoto, T. Nozaka, and M. Nohara: J. Phys. Soc. Jpn. **80** (2011) 093704.
- 19) N. Ni, J. M. Allred, B. C. Chan, and R. J. Cava: PNAS **108** (2011) E1019.
- 20) C. Löhnert, T. Stürzer, M. Tegel, R. Frankovsky, G. Friederichs, and D. Johrendt: Angew. Chem. Int. Ed. **50** (2011) 9195.